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Cloud Point Extraction and Spectrophotometric Determination of Thorium(IV) Ions and their Application in Silicate Rock Samples

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ABSTRACT

The phase-separation phenomenon of non-ionic surfactants occurring in aqueous solution was used for the extraction and concentration of thorium ions. The method is based on the complexation reaction of thorium(IV) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) at pH (3.4). The formed complex was quantitatively extracted to the phase rich in octylphenoxypolyethoxyethanol (Triton X-114) after centrifugation. The enriched analyte in the surfactant-rich phase was extracted, dissolved and determined spectrophotometrically at 531 nm. The optimal extraction and reaction conditions (e.g. pH, surfactant concentration, reagent concentration, temperature, effect of time) were evaluated and the analytical characteristics of the method (e.g. limit of detection, linear range and preconcentration factor) were obtained. Linearity was obeyed in the range of 0.125-2.5µg/ml of Th(IV). The interference effect of some foreign ions was also tested. The proposed method was successfully applied for the preconcentration and determination of trace thorium ions in certified reference sample and silicate geological samples.

Introduction

Thorium is a heavy metal that naturally abundant and distributed in a small amount in most rocks and soils. The average abundance in the earth's crust is 10 to 20 ppm. It is an important radioactive element, not only has extensive application in industry, e.g., optics, radio, gas mantle, aeronautics and aerospace, metallurgy and chemical industry, but is also used as nuclear fuel energy for electricity production in power plants [1].

In view of the extensive application, toxicity and hazard effects, the development of reliable methods for the separation and monitoring of thorium in various samples is of particular significance. In fact, direct determination of Th(IV) is still difficult, owing to its low concentrations and matrix effects.

Several preconcentration and separation techniques have been employed for this purpose, including liquid–liquid extraction [2,3], electrodeposition [4], ion exchange [5], extraction chromatography [6,7] and solid-phase extraction (SPE) [8,9].

Cloud-point extraction (CPE) is a versatile and simple method for the preconcentration and extraction of hydrophobic species from aqueous solution. This technique is based on the property of most non-ionic surfactants in aqueous solutions to form micelles and become turbid when heated to a temperature known as the cloud point temperature. Above cloud point temperature, the micellar solution separates into a surfactant-rich phase of a small volume and a diluted aqueous phase. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, speedy and of lower toxicity to the environment than those extractions that use organic solvents [10].

A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio, thus improving its concentration factor. In CPE technique, both surfactant and chelating agent are critical in attaining highest extraction percentages. The surfactants which are used in cloud point extraction are mostly of nonionic type, such as Triton X-114 (polyoxyethylene7.5-octylphenoxy ether) [11,12], Triton X-100 (polyoxyethylene-9.5-octylphenoxy ether) [13], PONPE (polynonylphenyl ether) [14] or mixtures of nonionic and cationic/anionic [15].

Among various organic ligands used in cloud point extraction, pyridylazo and thiazolylazo derivatives, such as 1-(2-pyridylazo)-2-naphthol (PAN) [16], 1-(2-thiazolyazo)-2-naphthol (TAN) [17], 4-(2-pyridylazo)

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resorcinol (PAR) [18], 2-(5-bromo2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP) [19] have been widely employed due to their low solubility in water and capacity to form complexes with a large variety of metals. Other reagents used for cloud point extraction in several procedures are ammonium pyrrolidinedithiocarbamate (APDC), diethyldithiocarbamate (DDTC) [12], 2-amino-cyclopentene1-dithiocarboxylic acid (ACDA), O,O-diethyldithiophosphate (DDTP), 8-hydroxyquinoline (oxine, 8-HQ), and dithizone.

Few reports had been developed on the preconcentration of thorium(IV) by CPE method prior to its determination. Cloud point extraction was used for the preconcentration of Th(IV), after the formation of complex with 5-(2′,4′-Dimethylphenylazo)-6-hydroxy-pyrimidine-2,4-dione (DMPAHPD), and later analysis by UV-Vis spectrophotometry using CTAB/Triton X-100 [20]. Thorium(IV), uranium(VI), zirconium(IV) and hafnium(IV) were simultaneous preconcentrated after chelation with dibenzoylmethane (DBM) then were detected by inductively coupled plasma-optical emission spectrometry using Triton X-114 as surfactant [21]. A CPE procedure was investigated for the determination of Th(IV) by liquid scintillation counting (LSC) using tributyl phosphate (TBP) and Triton X-114 [22]. A mixed micelle-mediated CPE combined with UV–Vis spectrophotometry was proposed for determination of thorium ions using quinalizarin as chelating agent [23]. Preconcentration of thorium and uranium species in the surfactant rich phase of Triton X-114 was carried out by complexing them with trioctylphosphine oxide (TOPO) and N,N,N′,N′-tetraoctyldiglycolamide (TODGA) and determined spectrophotometrically with arsenazo(III) [24].

The main purpose of this study was to apply CPE as a pre-concentration step for extraction and spectrophotometric determination of Th(IV) in aqueous samples. In this work, 2-(5-bromo-2-pyridylazo)-5diethylaminophenol (5-Br-PADAP) was used as a chelating agent and Triton X-114 as a non-ionic surfactant.

Materials and Methods
Instrumentation
A double beam spectrophotometer model (Labomed, Inc. U.S.A.) was employed to record all the spectrophotometric measurements. pH meter model (Digimed, DM-21, England) was used for adjusting the pH of the solutions. A thermostat bath (GFL 1083, Germany), which was maintained at the desired temperature, was utilized for the experiments of cloud point temperatures. A centrifuge (Hermle Z36 HK, Germany) with 100 ml calibrated centrifuge tubes was used to accelerate the phase separation process. Absorption spectra in the IR region were recorded using a Fourier transform infrared spectrometer (FT-IR) on the wavenumber range $4000 - 400$ cm^{-1} (Thermo Scientific, NICOLET iS10, USA); this spectrometer was used to characterize the major functional groups of the formed complex.

Reagents and solutions
All reagents were of analytical reagent grade. The water utilized in all studies was double distilled. Stock solution of Th(IV) was prepared at a concentration of 1000 µg/ml by dissolving the appropriate amount of its nitrate salt in double distilled water containing a few drops of nitric acid. Working standard solution was obtained by dilution of the stock solution. Aqueous 0.5 % (v/v) of Triton X-114 solution (Fluka, Switzerland) was prepared by dissolving 0.5 ml of Triton X-114 in 100 ml of double distilled water. 0.05 % 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) solution was prepared by dissolution of 0.05 g of the reagent (Merck, Germany) in 100 ml of ethanol (98 %) then stored in amber bottle. Buffer solutions were prepared to adjust the solution pH value (phthalate-hydrochloric acid, glycine-hydrochloric acid, sodium acetate-hydrochloric acid). Stock solution of NaCl (0.6 M) by dissolving 3.506 g NaCl in double distilled water and diluting to 100 ml in a flask. N,N-dimethylformamide (DMF) was purchased from (Sigma–Aldrich) that used to decrease the viscosity of surfactant-rich phase. The solutions of various cations and anions used for the interference study were obtained from the respective high purity inorganic salts by proper dilution in double distilled water.

Cloud point extraction procedure
An aliquot of Th(IV) standard solution was transferred to a 25 ml centrifuge tube; 2.5 ml of buffer solution (sodium acetate-hydrochloric acid, pH 3.4) and 1 ml of 0.05 % 5-Br-PADAP solution were added. This was followed by the addition of 2.0 ml of a 0.5 % (v/v) of Triton X-114 solution and 2.5 ml of 0.6 M NaCl solution. The solution was taken up to the mark with double distilled water. Subsequently, the solution was left to stand in a thermostatic water bath for 15 min at 55°C before centrifugation.

Separation of the aqueous and surfactant-rich phases was accelerated by centrifugation for 20 min at 5000 rpm. The mixture was cooled in an ice-salt bath to increase the viscosity of the surfactant-rich phase, and the aqueous phase was easily decanted by simply inverting the tube. Later, in order to decrease the viscosity and facilitate sample handling, 5 ml of DMF was added to the surfactant-rich phase and transferred to a quartz cell for an absorbance measurement at 531 nm.

Samples preparation
The samples that used in the application were subjected to major elemental analysis using standard methods of analysis [25], **Table 1.** Trace elements were determined using ICP-AES technique at ACME lab, Canada.

A 0.5 g of each powdered sample (200 mesh) was mixed with 20 ml of 6 M HNO$_3$ for two hours with shaking in water bath at a temperature up to 90°C. The produced solution was filtered and diluted with double distilled water to 25 ml [26].

To the residue, 20 ml of concentrated hydrofluoric acid solution, 10 ml concentrated perchloric acid and 5 ml concentrated nitric acid were added and heated till dryness

in a Teflon beaker. The digested cake was dissolved and warmed gently in 10 ml of dilute hydrochloric acid (1:1) then diluted to the required volume with double distilled water [27].

Results and discussion

The yield of CPE is dependent on various factors including, concentration of surfactant, concentration of reagent, electrolyte concentration, temperature and pH. So as to achieve maximum efficiency, absorbance and sensitivity, the aforementioned factors was investigated, and optimum conditions were determined.

The absorption spectra of both 5-Br-PADAP reagent and Th(IV)-5-Br-PADAP complex were illustrated in **Fig. 1**. Maximum absorbance of 5-Br-PADAP was attained at λ_{max} 445 nm. However, the extracted complex of Th(IV) was appeared at λ 531nm.

Optimization of experimental conditions
Effect of pH

The effect of pH on the absorbance of Th-5-Br-PADAP complex by addition of diluted NaOH or HNO_3 was studied. Series of experiments were investigated in the pH range 2.0-6.0. Thorium(IV), 5-Br-PADAP reagent, Triton X-114 and NaCl concentrations were kept constant at 1µg/ml, 0.05 %, 0.5 % and 0.2 M receptively. The obtained results, **Fig. 2**, showed that maximum absorbance was obtained at pH 3.4. At pH values higher than 3.4, the hydrolysis reaction played a dominant role. The hydrolysis of Th(IV) would occur prior to their chelation with 5-Br-PADAP, which lead to lower extraction efficiency. At pH < 3.4, only part of the Th(IV) was extracted into the surfactant-rich phase due to the incomplete formation of Th(IV)-5-Br-PADAP complex. Hence, pH 3.4 was chosen as the working pH [28].

Table 1: Chemical analysis of the major and trace elements of the samples

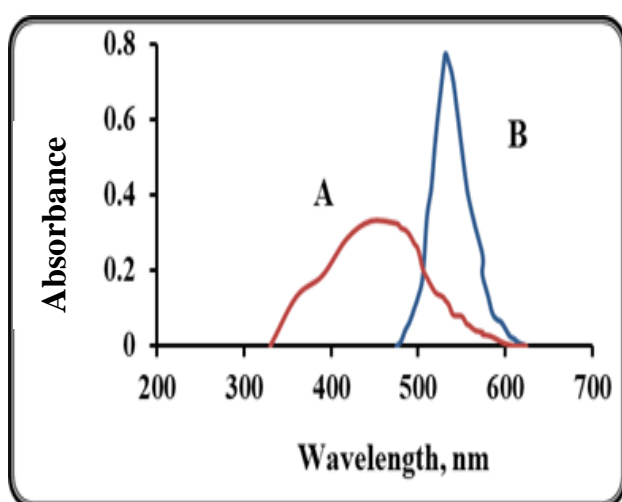| Sample NO. / Oxides %	1	2	Sample NO. / Trace element (µg/ml)	1	2
SiO_2	73.6	81.2	Cd	0.04	0.02
Al_2O_3	12.3	9.1	Co	0.8	0.8
TiO_2	0.05	0.02	Au	< 0.1	< 0.1
Fe_2O_3	1.27	0.37	Cu	3.95	6.4
CaO	0.6	1.5	V	3.0	1.0
MgO	0.3	0.03	Bi	0.3	0.17
Na_2O	5.8	2.2	Sb	0.04	0.07
K_2O	5.4	5.1	Eu	0.4	0.5
P_2O_5	0.07	0.005	La	20	8.9
			Pr	6.9	5.0

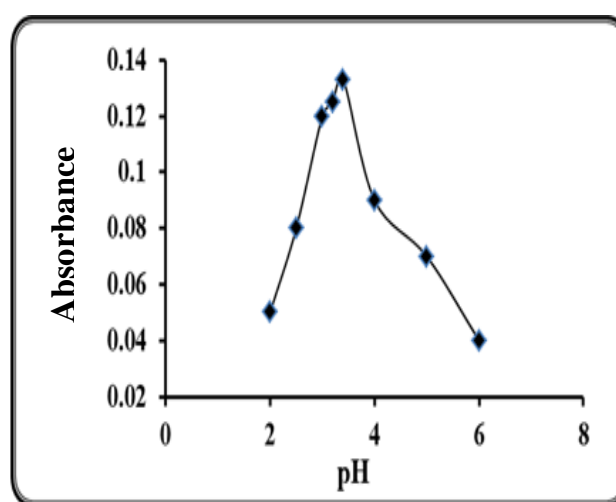**Fig. 1 :** Absorption spectra of (A) 5-Br-PADAP, (B) Th(IV) -5-Br-PADAP complex.

Fig. 2: Effect of pH on the absorbance intensity of the complex.

Effect of buffer type

The effect of buffer type on the absorbance intensity was studied using phthalate-hydrochloric acid, glycine-hydrochloric acid and sodium acetate-hydrochloric acid (Walpole). The other studied factors were fixed. It was found that Walpole buffer was the most effective one, **Table 2**.

The results showed that, above 2.5 ml of buffer solution in 25 ml (sodium acetate / HCl), no obvious variation took place in the absorbance. Therefore, it was revealed that 2.5 ml of buffer solution was adequate to form the complex and obtain maximum absorbance.

Effect of 5-Br-PADAP concentration

The effect of varying 5-Br-PADAP concentrations on the absorbance intensity of the formed complex was examined in the range 0.03-0.07 % on a solution containing (1 µg/ml Th(IV), 2.5 ml buffer solution, 0.5 % Triton X-114, 0.2 M NaCl) and subjected to the cloud point extraction process. **Fig. 3** showed that the absorbance increased by increasing reagent concentration up to 0.05 % then decreased at high concentrations, due to the increase in the background absorbance caused by further increasing amount of the ligand [29] or because utilizing a higher concentration of ligand causes more volume of organic as solvents that can prevent the micelle formation and reduce the extraction efficiency [30]. Therefore, 0.05 % of 5-BrPADAP was chosen as the optimum concentration. It was found that 1 ml of 0.05 % 5- Br-PADAP reagent was sufficient to complete complexation of Th(IV). The stoichiometry of the formed complex was established

using the molar ratio method. The plot of absorbance versus the molar ratio of ligand to Th(IV), obtained by varying the ligand concentration, showed inflection at molar ratio 2.0, indicating that the stoichiometric ratio was (2 : 1) [5-Br-PADAP : Th(IV)]. As reported by other authors [31], the latter stoichiometric ratio is indicative of an octahedral complex. Hence, the suggested structure for the formed complex as shown in Scheme 1 [32].

Effect of surfactant concentration

Triton X-114 was chosen for the formation of the surfactant-rich phase because of its higher extraction efficiency as well as its lower cloud point temperature. The low cloud point temperature avoids back extraction during centrifugation [33].

The variation of the absorbance as a function of the concentration of Triton X-114 in the range of 0.2 – 0.7 % (v/v) was examined. As shown in **Fig. 4**, the absorbance of the solutions increased by increasing the surfactant concentration up to 0.5 % (v/v) then decreased. It can be explained that an increase in surfactant amount also increases the volume of the micellar phase that makes the concentration of the analyte in the enrichment phase decreases and the viscosity of the surfactant phase increases [12]. At lower concentrations, the extraction of metal chelate was found to be low because of an inadequacy in the assemblies to entrap the hydrophobic complex quantitatively [34]. Therefore, in order to achieve a good enrichment factor and high extraction efficiency, TritonX-114 concentration of 0.5 % (v/v) was chosen for subsequent experiments.

The effect of variation in the volume of 0.5 % solution of Triton X–114 was studied by keeping other reaction conditions at the optimum level. The results revealed that, the optimum volume of Triton X–114 was 2 ml.

Table 2: Effect of buffer type on the absorbance intensity of the complex

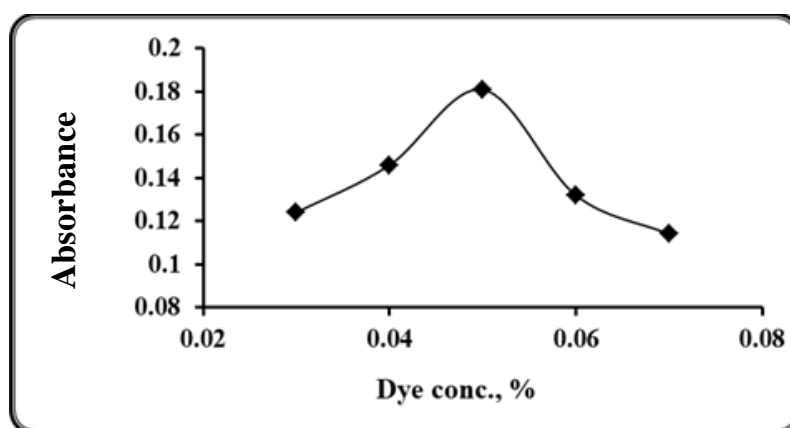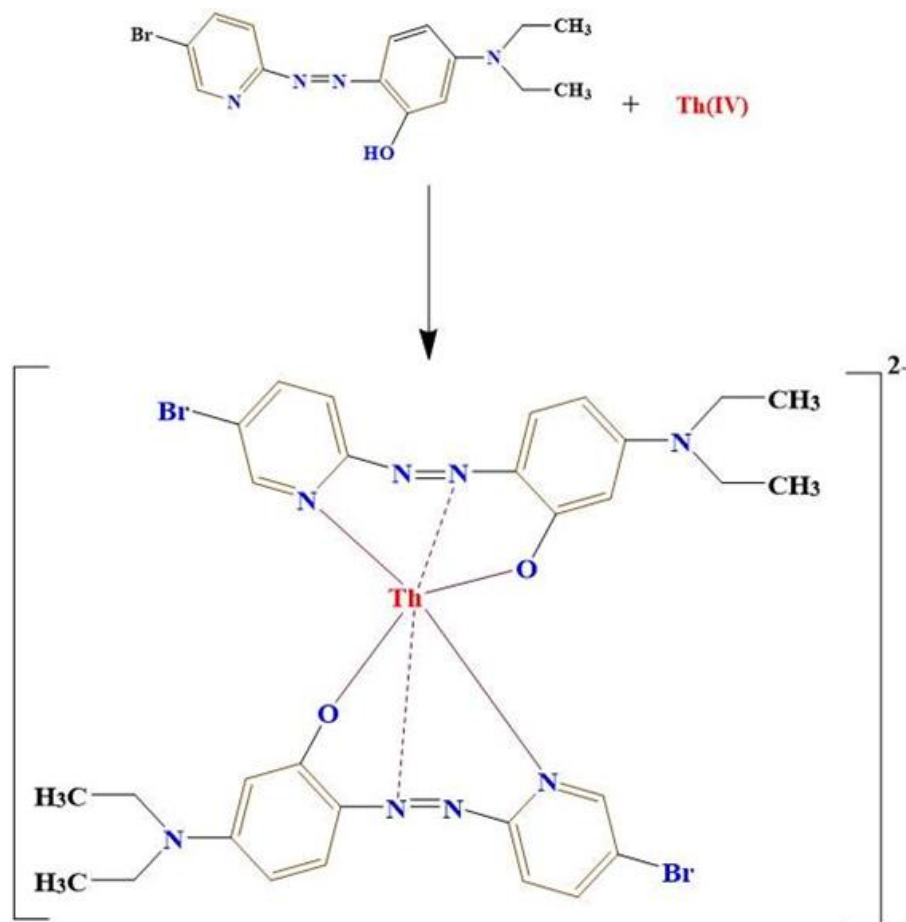| Buffer type	Absorbance
Glycine	0.090
Phthalate	0.112
Walpole	0.161

Fig. 3: Effect of dye concentration on the absorbance intensity of the complex.

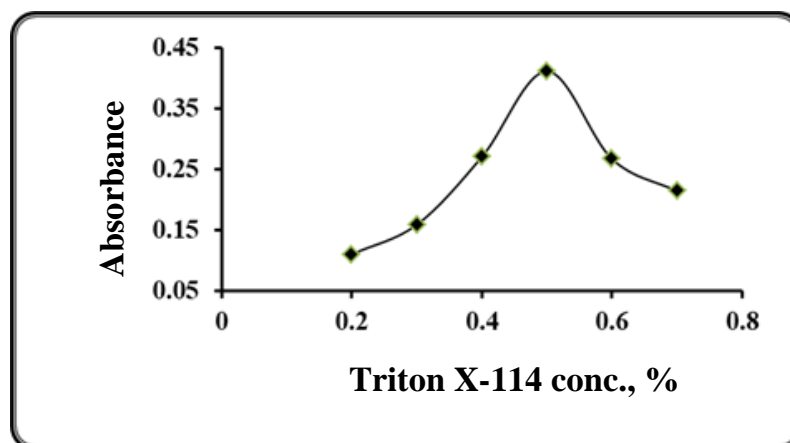**Scheme 1 :** The suggested structure of Th(IV)-5-Br-PADAPcomplex.

Fig. 4: Effect of Triton X-114 concentration on the absorbance intensity of the complex.

Effect of inorganic salts

Phase separation in CPE can be carried out by heating the mixture containing the surfactant above the cloud point temperature. However, very high temperature might lead to decomposition of the formed complex. Based on this, the salting-out effect was introduced as an alternative to induce the phase separation.

It was observed that the presence of electrolytes decreases the cloud point (salting-out effect), resulting in more efficient extraction. The lower cloud point extraction efficiency is attributed to electrolytes promoting dehydration of the poly(oxyethylene)chains [35]. According to Komaromy-Hiller *et al.* [36] the salting-out phenomenon is directly related to desorption of ions to the hydrophilic parts of the micelles, increasing interaction between micelles and consequently leading to the precipitation of surfactant molecules. The presence of salt can increase the incompatibility between the water structures in the hydration shells of analytes and surfactant macromolecules, which can reduce the concentration of "free water" in the surfactant-rich phase and, consequently, reduce the volume of the phase [37].

Based on that argument, the salting out effect was studied in the presence of different electrolyte salts of NaCl, Na_2SO_4, KCl and KI. The obtained results illustrated in **Table 3** proved that NaCl was the best for this target; NaCl was investigated in the concentration range 0.1-1.0 M. The data illustrated in **Fig. 5**, revealed that the highest absorbance was obtained at 0.6 M NaCl. At higher concentration than 0.6 M, the absorbance decreased considerably. This effect might be explained by the additional surface charge when the NaCl concentration was very high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process. High concentration of the salt can increase the density of water drops accompanied by the surfactant rich phase, and hence disturb the phase separation. [30]. Therefore, 0.6 M NaCl concentration was used in all further experiment.

The influence of NaCl amount ranging from 1.0 to 3.5 ml was investigated in which the other experimental variables remained constant. It was observed that the optimum volume of NaCl was 2.5 ml. Thus, 2.5 ml of 0.6 M NaCl was used for subsequent experiments.

Effect of equilibration temperature and incubation time

To achieve easy phase separation and preconcentration as efficient as possible, optimal incubation time and equilibration temperature are necessary to complete reactions. It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of

extraction and efficient separation of phases.

Lindman and Wennerström [38] stated that the mechanism of phase separation is due to an increase in the micellar aggregation number when temperature is increased. It may be caused by a change in micellar interactions, which are repulsive at low temperatures but predominantly attractive at high temperatures. This can be explained on the basis of the dehydration process that occurs in the external layer of the micelles of non-ionic surfactants when temperature is increased [39]. The dielectric constant of water is also decreased by increasing temperature, rendering it to a poorer solvent for the hydrophobic portion of the surfactant molecule [40]. Therefore, the phase volume ratio of all non-ionic surfactants decreases as the equilibration temperature increases. The greatest analyte enrichment factors are, thus, expected where the CPE is conducted using equilibration temperatures that are well above the cloud point temperature of the surfactant [41].

The influence of equilibration temperature was investigated in the range 30 - 65°C. The obtained results, **Fig. 6** indicated that the equilibration temperature of 55°C was sufficient for the separation process. Above this temperature, a decrease in the extraction efficiency was found due to the decomposition of the formed complex.

The dependence of extraction efficiency upon incubation time was also studied for a time interval of 5 – 25 min. An incubation time of 15 min was selected as the best to obtain quantitative extraction.

Table (3): Effect of salt type on the absorbance intensity of the complex

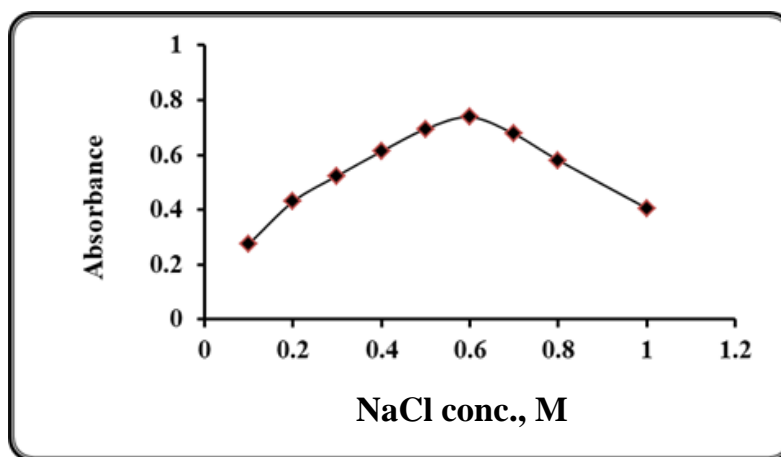| Salt type	Absorbance
NaCl	0.450
KI	0.362
KCl	0.157
Na_2SO_4	0.080

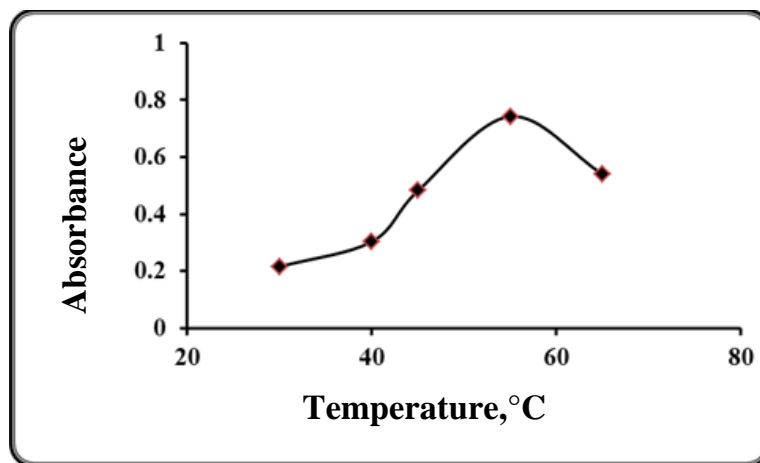**Fig. 5:** Effect of NaCl concentration on the absorbance intensity of the complex.

Fig. 6: Effect of temperature on the absorbance intensity of the complex.

Effect of centrifugation rate and time

In general, centrifugation time hardly ever affects micelle formation but accelerates phase separation in the same time as in conventional separations of a precipitate from its original aqueous environment. The effects of centrifugation rate and time were evaluated in the range of 3000-6000 rpm and 5 - 25 min, respectively. A centrifugation rate of 5000 rpm and centrifugation time of 20 min were selected for the entire procedure as shown in **Fig. 7 & 8**, since complete separation occurred for this time and rate and no appreciable improvements were observed for longer times and rates.

Effect of the order of addition of reagents

During the course of investigation, it was found that the sequence of addition of reagents was also important. Thus, different orders of the reagent's addition were studied using optimized amounts of reagents (2.5ml buffer, 0.05 % 5-Br-PADAP, 0.5 % Triton X-114, 0.6 M NaCl). Based on the data shown in **Table 4**, it was observed that the best order of reagent addition was: Th(IV), buffer solution (3.4), 5-Br-PADAP reagent, Triton X-114, NaCl solution. While, other sequences gave lower values of absorbance compared to the above sequence. Best results of absorbance obtained as buffer solution was added before ligand (A) to create the optimum pH for complex formation.
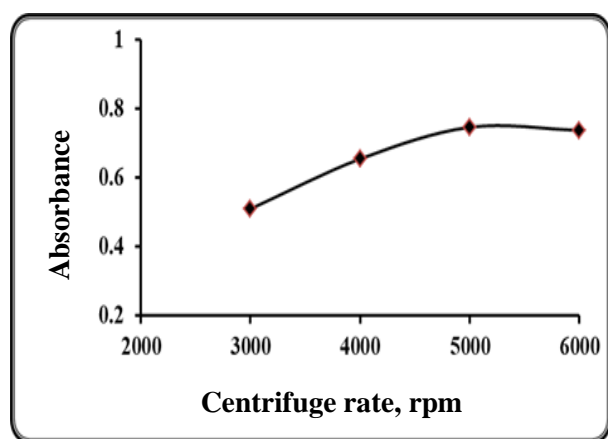

Fig. 7: Effect of centrifuge rate on the absorbance intensity of the complex.
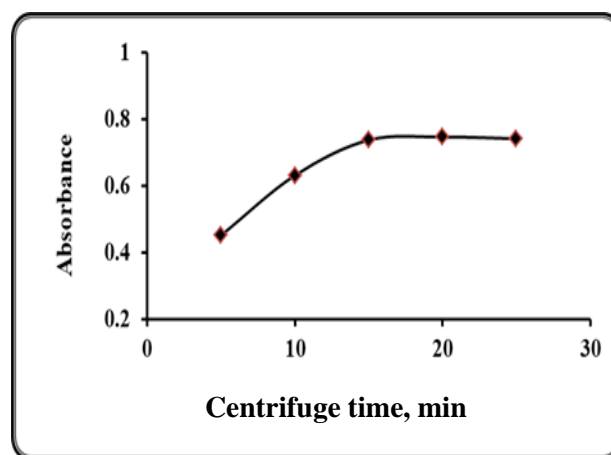

Fig. (8): Effect of centrifuge time on the absorbance intensity of the complex.

Table 4: Effect of order of addition on the absorbance intensity of the complex

Sequence of number	Sequence of addition	Absorbance
A	M+B+L+TX+NaCl	0.744
B	M+L+B+TX+NaCl	0.685
C	M+B+TX+L+NaCl	0.531

Metal (M), Buffer (B), Ligand (L), Triton X-114 (TX)

Effect diluting agent

In order to decrease the viscosity of surfactant-rich phase and facilitate its transfer into a spectrophotometric cell and absorbance measurements, three solvents namely, ethanol, methanol and dimethylformamide (DMF) were tested as diluents. The data featured in **Table 5** showed that, DMF was the proper diluting agent. The optimum conditions of CPE are summarized in **Table 6**.

Interference studies

The effect of foreign ions on the determination of Th(IV) by the proposed method was investigated by measuring the absorbance of the solutions containing 0.5 µg/ml of Th(IV) in the presence of various concentrations of other ions. The tolerance limit was defined as the concentration of added ion that caused less than ± 5 % relative error in the determination of Th(IV). The foreign ions can be tolerated at the levels given in **Table 7**. Most of the coexisting ions do not interfere with the extraction and determination of Th(IV), and some of them (Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}) are tolerated at high levels. However, uranyl ion and Fe^{3+} were interfered at low concentrations. Thus, the interfering effect of these ions was compensated in the presence of EDTA 0.1 % (w/v) as a proper masking agent.

Table 5: Effect of diluting agent type on the absorbance intensity of the complex

Diluting agent	Absorbance
Ethanol	0.362
Methanol	0.491
DMF	0.746

Table 6: The optimized conditions for Th(IV) determination using CPE method

Conditions	Value
pH	3.4
Buffer type	Sodium acetate-HCl
5-Br-PADAP concentration, %	0.05
Triton X-114 concentration, (%, v/v)	0.5
NaCl concentration, M	0.6
Equilibrium temperature, (°C)	55
Equilibrium time, (min)	15
Centrifuge time, (min)	20
Centrifugation rate, (rpm)	5000
Diluent type	Dimethylformamide

Table 7: Tolerance limit of foreign ions on the determination of Th(IV)

Foreign ions	Tolerance limit, ng ml^{-1}
Na^+	2000
Al^{3+}	6000
Mg^{2+}, Ca^{2+}, Ti^{4+}	1000
K^+	750
Cu^{2+}	80
Mn^{2+}, La^{3+}, Cd^{2+}	40
UO_2^{2+}, Ni^{2+}, Co^{2+}	10
Fe^{3+}	5
NO_3^-	20000
Cl^-	10000
CO_3^{2-}	2000
SO_4^{2-}	200

Analytical characteristics

The calibration curve was constructed by preconcentrating 25 ml of standard solutions containing known amounts of the analyte in the presence of 5-Br-PADAP and Triton X-114 for CPE of Th(IV), and under the experimental conditions specified in the general procedure. Linear relationship between the absorbance measured and the concentration of the metal in solution was obtained as shown in **Fig. 9**. Linearity was maintained between 0.125-2.5 µg/ml for the equation A= 0.7021C+0.0039, where A= absorbance and C= concentration of the analyte. **Table 8** lists the analytical characteristics, including regression equation, linear range, limits of detection and quantification, Sandell's sensitivity and reproducibility. The detection limit (LOD) and limit of quantitation (LOQ), for the proposed method was evaluated using the formula:

LOD = 3.3 x σ/S

LOQ = 10 x σ/S

Where, σ = the standard deviation of the blank

S = the slope of the calibration curve

The high value of molar absorptivity (ε) and low values of Sandell's sensitivity and LOD indicate the high sensitivity of the proposed method. The relative standard deviation (R.S.D.) for seven replicate measurements of 1 µg/ml of Th(IV) was 1.44 %. The preconcentration factor, calculated as the ratio between the volume of the aqueous phase and the final volume of the surfactant-rich phase. Further preconcentration factor was also feasible, either by increasing the amount of the sample solution or/and by suitably decreasing the amount of the diluting agent. Thorium ions could be enriched to 25 times. A comparison of the characteristic data of the present method with those of some other reported spectrophotometric methods for the determination of Th(IV) was given in **Table 9**, The higher sensitivity of the proposed method was notable and greater than that of other methods.
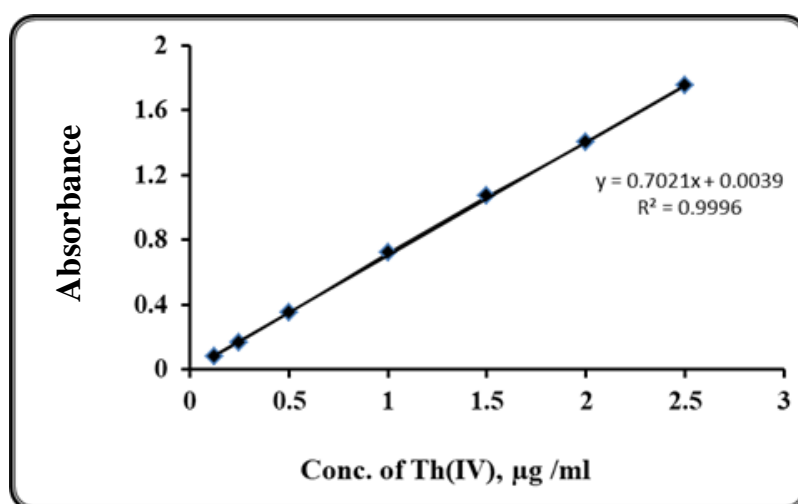

Fig. 9: Calibration curve of Th(IV)-5-Br-PADAP complex.

Table 8: Analytical characteristics of the proposed method.

Parameter	Value
λ_{max}	531
Linearity range (µg ml^{-1})	0.125-2.5
Regression equation Y*	Y=0.7021X+0.0039
Slope	0.7021
Intercept	0.0039
Correlation coefficient (r)	0.9996
Molar absorptivity (l mol^{-1} cm^{-1})	1.63×10^5
Sandell's sensitivity (µg cm^{-2})	0.0014
Detection limit (µg ml^{-1})	0.017
Quantification limit (µg ml^{-1})	0.05
Reproducibility (RSD, %) (n = 7)	1.44

* y=ax+b, where x is the concentration of analyte in µg/mL and y is the absorbance

Table 9: Comparison of the present method with other spectrophotometric methods for the determination of Th(IV)

Reagent	$\lambda_{(max)}$ nm	Molar absorptivity $\varepsilon \times 10^5$ l mo1^{-1} cm^{-1}	Detection limit µg ml^{-1}	Sandell's sensitivity µg cm^{-2}	Reference
1-(2′-Thiazolylazo)-2-naphthol	555	0.314	0.15	0.0074	42
Disodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo) benzene arsonic acid	544	0.169	1.5	0.082	43
Bromocresol orange	550	0.928	0.15	0.0025	44
2,3,4-Trihydroxyacetophenoneoxime	325	0.317	1.2	0.0073	45
Chrome azurol-S and cetyldimethylethylammonium bromide	640	0.855	0.12	0.0029	46
thorin / cetylpyridinium chloride	581	0.295	1.0	0.0068	47
2-hydroxy-3-methoxybenzaldehyde isonicotinoyl hydrazone	395	0.14	0.15	0.016	48
5-Br-PADAP	531	1.63	0.01	0.0014	Present method

Fourier transformation infrared spectra (FTIR) analysis

The infrared spectra of 5-Br-PADAP and Triton X-114 and their complex with thorium ions were carried out as shown in **Fig. 10**. There was a noticeable change in the spectra of the complex from that of free reagents in term of position and intensities of peaks. The weak bands which observed at 3051 cm^{-1} in the ligand spectrum is due to (C─H) aromatic. The peak appeared at 1650 cm^{-1} due to (C=N) stretching vibration for 5-Br-PADAP was shifted to 1639 cm^{-1} for the chelate. In addition, the peak appeared at 1391 cm^{-1} due to (N=N) stretching vibration of Br-PADAP was shifted to 1379 cm^{-1}. On the other hand, the broad band that observed at 3445 cm^{-1} was attributed to (O–H) stretching vibration. This band was shifted to 3390 cm^{-1} with increase in band intensity in the spectrum of the complex. This indicates that the thorium ions have been coordinated with non-bonding electron pairs of nitrogen in Br-PADAP and its hydroxyl group also involved in the interaction [49].

Application

The accuracy of the developed method was examined by determining thorium species in certified reference rock sample (DL-1a). The results of these determinations are given in **Table 10**. Good agreement between the obtained results and the certified values indicates the successful application of the present method for the determination of thorium ions in these real samples. In order to validate the proposed methodology, the developed procedure was applied to the determination of thorium ions in silicate geological samples. These samples were collected from Wadi Sikait, South Eastern Desert, Egypt. For this purpose, an aliquot of samples was preconcentrated following the proposed procedure. The performance of the proposed method was assessed by calculation of the t value (for accuracy) and F test (for precision) compared with ICP method. The mean values were obtained in Student's t and F tests at 95 % confidence limits. The results showed that the calculated values **Table 10** did not exceed the theoretical values.
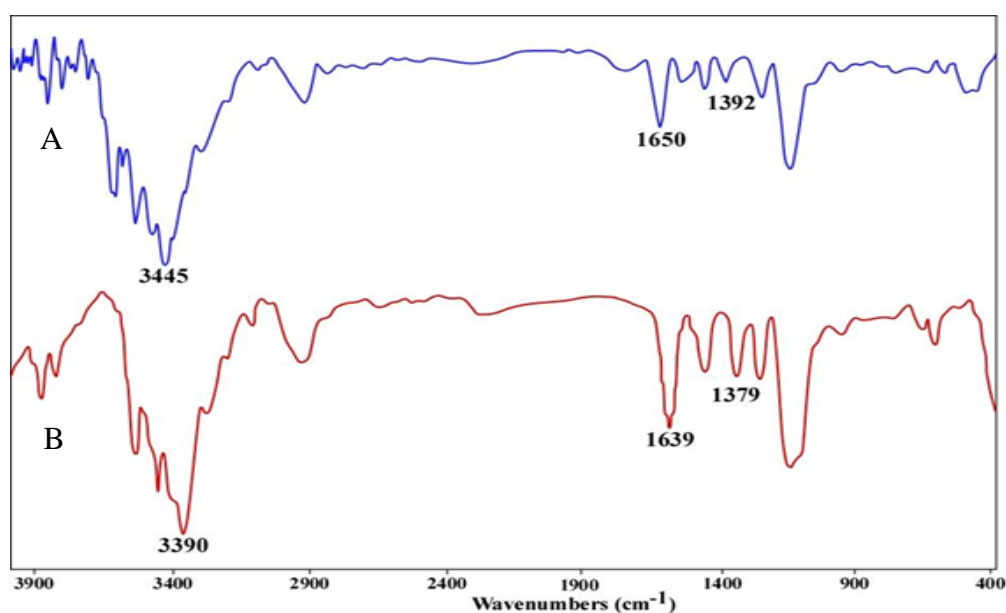

Fig. 10: The FTIR spectra of (A) the ligand, (B) the formed complex with Th(IV).

Table 10: Determination of Th(IV) in certified and geological silicate samples using the developed procedure

Reference sample	Certified Concentration (µg/ml)	Measured Concentration (µg/ml)	RSD (%)
DL-1a	76	75.4	1.5
Rock sample	**ICP-MS Conc. (µg/ml)**	**CPE-UV-Vis Conc. (µg/ml)**	**RSD (%)**
1 (t and F test) [a]	36.4	36.1 (0.55, 1.16)	1.77
2 (t and F test) [a]	24.3	23.9 (0.47, 1.94)	2.26

[a] Theoretical value for t and F values for three degrees of freedom and 95 % confidence limits are 3.182 and 19, respectively.

Conclusion

The combined advantages of the cloud point methodology (easy, safe, rapid and inexpensive) and the use of 5-Br-PADAP as a sensitive chromogenic reagent for thorium(IV) was utilized for its determination in rock samples. Triton X-114 was chosen for the CPE due to its excellent physicochemical characteristics, low cloud point temperature, high density of the surfactant-rich phase. It facilitates phase separation by centrifugation, as well as its commercial availability and relatively low price and low toxicity. The proposed method is suitable for the preconcentration of thorium species prior to their determination by spectrophotometry. In this method, a low limit of detection and good precision (low RSD %) were obtained. The method has been successfully applied to the determination of Th(IV) in certified and geological silicate samples.

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